

## LA-UR-15-25978

Approved for public release; distribution is unlimited.

Title: First Row Transition Metal Adsorption on Actinide Resin

Author(s): Daum, Jaimie Kay

Intended for: Report

Issued: 2015-07-29 (Draft)

---

**Disclaimer:**

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

# First Row Transition Metal Adsorption on Actinide Resin

Jaimie Daum

## 1. Introduction

Actinide resin is an extraction chromatographic resin that is commercially available from Eichrom Technologies, LLC. The resin is based upon the extractant bis(2-ethylhexyl)methanediphosphinic acid ( $H_2DEH[MDP]$  or "DIPEX®") (Figure 1), which is supported on the inert polymeric substrate Amberchrom CG-71ms acrylic resin beads<sup>1</sup>. Actinide resin displays extremely high extraction coefficients for metals with oxidation states +3 and above.

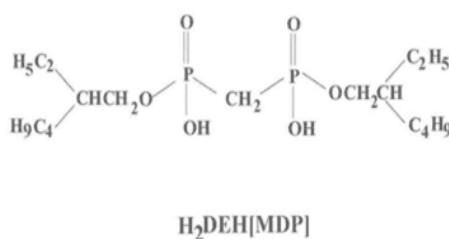


Figure 1: DIPEX® Extractant

The DIPEX® extractant has four different coordination sites for binding to a metal: two neutral phosphoryl ligand sites and two hydroxyl sites that require deprotonation prior to binding to a metal. The selectivity of the DIPEX extractant system is due to a combination of electrostatic and steric effects. The diposphonic acid ligands of the extractant system are not attached to a rigid polymeric network and therefore can easily rearrange and coordinate around target ions. Therefore, the complexing ability of the ligand to various metals in the periodic table is complicated.

Actinide resin has been characterized for the retention of actinides and non-actinide metal ions found within environmental samples (Figures 2 and 3). The retention of both actinides and non-actinide metal ions is very strong up to pH 2, after which the retention diminishes with increasing acid concentration. The resin has an unusually strong retention for Am(III) below 1M HCl; and the  $k'$  of the metal ion at its lowest capacity still remains near  $10^3$  even though the capacity declines rapidly. The lanthanides are suspected to behave similarly to Am(III) within separation schemes.

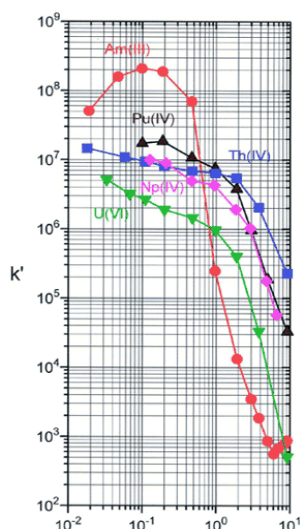


Figure 2:  $k'$  values for actinide species on Actinide Resin in varying concentrations of HCl, 1 h equilibration time, 22 °C.<sup>1</sup>

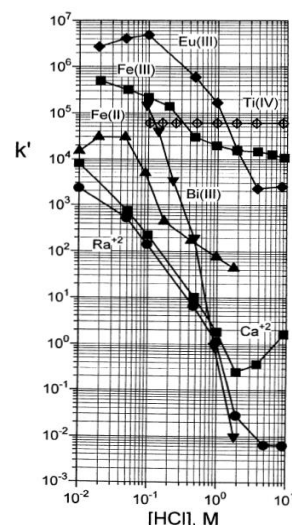
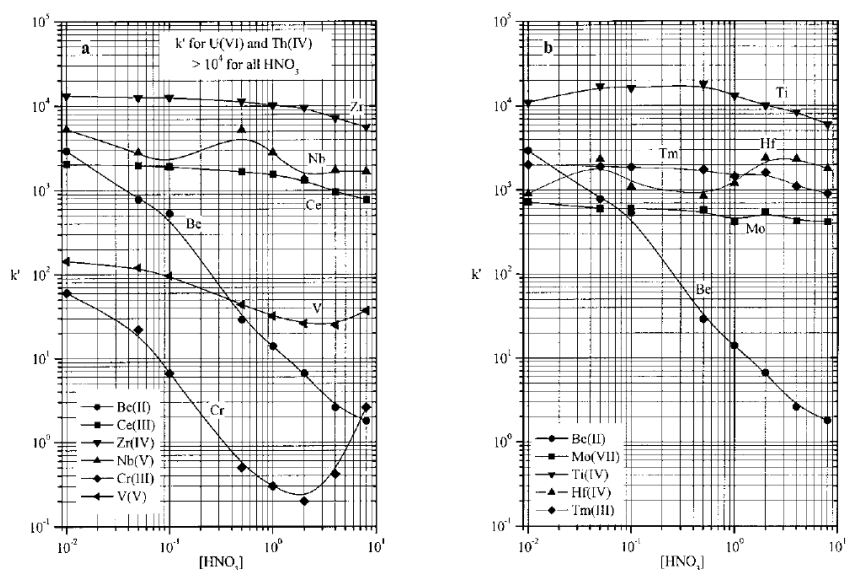


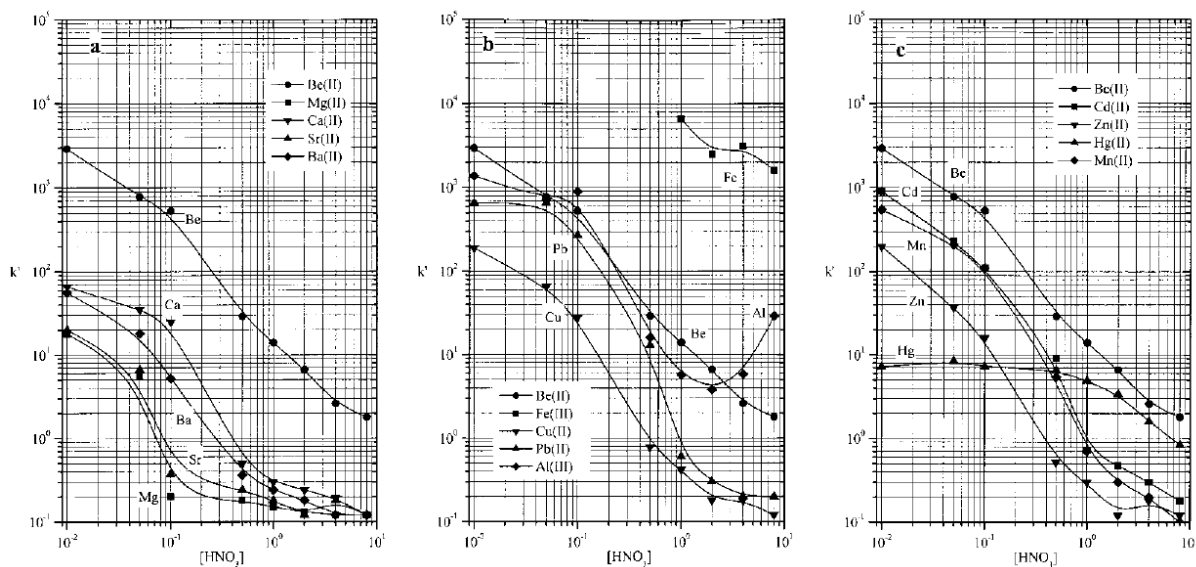
Figure 3:  $k'$  values for non-actinide metal ion adsorption on Actinide Resin in varying concentrations of HCl, 1 h equilibration time, 22 °C.<sup>1</sup>

Actinide resin has also been examined for the separation of Be(II) from a range of elements that either could interfere with its determination by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or that commonly occur in environmental samples. The effect of potential ICP-AES spectral interferences on the uptake of Be(II) on the DIPEX® extractant was studied (Figure 4). Be(II) is strongly retained below 0.1 M HNO<sub>3</sub>, while most of the potential spectral interferences ( Zr(IV), Nb(V), Ce(III), Ti(IV), Hf(IV), Tm(III), Mo(VII), U(VI), and Th(IV)) were strongly retained over the entire acid range studied<sup>2</sup>.

The effect of potential matrix interferences from environmental samples on the uptake of Be(II) on the DIPEX® extractant was studied (Figure 5). The resin had a high selectivity for Be(II) compared to other alkaline earth metal ions (Figure 5a). Therefore, the presence of Ca(II) within a sample would not significantly affect the retention of Be(II) on the resin. Cu(II), Hg(II), An(II), Mn(II), and Cd(II) are weakly retained on the resin compared to Be(II), while Fe(III) is strongly retained over the entire acid range studied (Figure 5b and 5c). Pb(II) and Al(III) had similar retention profiles to that of Be(II); therefore, large amounts of these metal ions within the sample could interfere with the uptake of Be(II) on the resin<sup>2</sup>.



**Figure 4:**  $k'$  values for Be(II) and potential ICP-AES spectral interferences in varying concentrations of HNO<sub>3</sub>, 1 h equilibration time, 22 °C.<sup>2</sup>



**Figure 5:**  $k'$  values for Be(II) and potential matrix interferences in varying concentrations of HNO<sub>3</sub>, 1 h equilibration time, 22 °C.<sup>2</sup>

## 1.1 Extraction Chromatography

Extraction chromatography is one of the main radioanalytical separation techniques that is utilized to separate radionuclides from a wide variety of sample matrices. This technique incorporates the favorable selectivity associated with the organic compounds used in solvent extraction with the multistage character and ease of operation of a chromatographic process<sup>3</sup>. Extraction chromatographic resins are comprised of beads with three main components: an inert support that is usually porous silica, a stationary phase comprised of liquid extractants, and a mobile phase that consists of a mineral acid solution<sup>4</sup>. The selective extraction of the radioisotope of interest is followed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) to determine the retention capability of the resin.

The retention capability of the resin is measured by the retention factor,  $k'$ , which is the free column volumes to peak maximum. The retention factor is indirectly determined from the weight distribution factor,  $D_w$ , which is the metal ion concentration per gram of resin from a given volume of aqueous solution:

$$D_w = \frac{A_0 - A_s}{A_s} \cdot \frac{\text{mL}}{\text{g}} \quad (1)$$

where  $A_0$  is the initial metal concentration in the aqueous solution,  $A_0 - A_s$  is the metal concentration that was sorbed onto a known weight of resin (g), and  $A_s$  is the metal concentration in the aqueous solution in a known volume (mL). The retention factor can be related to the weight distribution ratio if the free column volume (FCV) is determined for an amount (g) of the specific resin being used (The free column volume per gram of Actinide Resin is 1.90):

$$k' = D_w / \left( \frac{\text{FCV}}{\text{g}} \right) \quad (2)$$

## 1.2 Post-Detonation Debris

Nuclear Forensics is the analytical characterization and evaluation of nuclear materials that are either intercepted in a pre-detonation state or retrieved from post-detonation debris and fallout. The characterization and evaluation conducted on the confiscated nuclear forensic evidence allows law enforcement and intelligence agencies to prevent, mitigate, and attribute radiological or nuclear incidents. Post-detonation debris is a unique environmental sample formed under extreme conditions. The composition of the post-detonation debris is dependent upon the weapon design, height of the blast, and the surface composition of the detonation site. The detonation of a nuclear weapon produces extremely hot weapon residues that radiate large amounts of energy, forming an extremely hot and highly luminous fireball. The residual radiation from an air burst detonation, in which the fireball does not come into contact with the surface of the earth, is mainly comprised of the fission products produced and, to a lesser extent, the un-fissioned plutonium and uranium nuclear material. An air burst detonation produces less fallout compared to a surface burst detonation, in which the fireball comes into contact with the surface of the earth and forms a crater due to the vaporization of the earth, water, air, and other substances in the explosion environment. The residual radiation from a surface burst detonation is induced by the interaction of neutrons with elements that are present within the vaporized material in the explosion environment<sup>5</sup>. Post-detonation forensics requires innovative radioanalytical techniques such as extraction chromatography in order to isolate, characterize, and determine the nuclear material within the debris. Matrix constituents, including the first row transition metals, could inhibit these radioanalytical techniques and subsequent determination by ICP-AES.

## 1.3 Research Goals

The research focuses on further characterizing Actinide Resin for the first row transition metals that could be found within post-detonation debris or could interfere with ICP-AES analysis. No research has been published on

the adsorption of most of first row transition metals on Actinide Resin in a hydrochloric acid system. Published research also has not included the absorption of Co(II) or Ni(II) on Actinide Resin in a nitric acid system.

## **2. Methodology**

### **2.1 Reagents**

Ultrapure water ( $18\text{ M}\Omega\text{ cm}^{-1}$ ) (MilliQ 50, Bedford, MA, USA) was used for the preparation of all solutions. All reagents were trace metal grade (Fisher Scientific, Hampton, NH, USA) and used as received without further purification. Actinide Resin was purchased from Eichrom Technologies, LLC (Lisle, IL, USA).  $\text{CoCl}_2$  (Alfa Aesar, Ward Hill, MA, USA),  $\text{CrCl}_3$  and  $\text{ZnCl}_2$  (Acros Organics, Geel, Belgium, Germany),  $\text{MnCl}_2$  and  $\text{CuCl}_2$  (SPEX Industries (Metuchen, NJ, USA), and  $\text{NiCl}_2$  (Fisher Scientific, Hampton, NH, USA) were used as received. Acid solutions were titrated with either 0.1 N or 1.0 N potassium hydroxide (BDH Chemicals, Radnor, PA, USA) using 0.5% phenolphthalein as the indicator. Batch contact studies were performed using 2 mL Empty Bio-Spin Chromatography Columns (Biorad Laboratories, Hercules, CA, USA). All measurements were performed using a Thermo Scientific iCAP 7000 Series ICP-OES (Waltham, MA, USA).

### **2.2 First Row Transition Metal Salt Solutions**

5mM Cr(III), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) solutions were prepared by dissolving the respective salts in 0.01, 0.1, 0.5, 1.0, 2.0, 4.0, 8.0, and 10.0 M hydrochloric acid. 5 mM Co(II) and Ni(II) solutions were prepared by converting/ dissolving the respective salts in 0.01, 0.1, 0.5, 1.0, 2.0, 4.0, 8.0, and 11.0 M nitric acid.

### **2.3 Batch Contact Studies**

Bio-Spin Columns (2 mL) were filled with  $0.0500 \pm 0.0005\text{ g}$  Actinide Resin. The resin was preconditioned with 1.30 mL of the desired acid concentration and agitated for one hour. The solution within each column was drained into a pre-weighed glass scintillation vial and titrated in order to determine the change in acid concentration due to the Actinide Resin having an affinity for the mineral acid. Each column was then “spiked” with 1.30 mL of the 5 mM transition metal solution in the desired acid concentration and agitated for one hour. The solution within each column was drained into a pre-weighed glass scintillation vial and the vial was re-weighed. For each transition metal studied, three replicates were conducted for each acid concentration along with a blank that contained no metal in the solution. Three resin blanks were also conducted for each transition metal studied in the lowest acid concentration in which the column contained no Actinide Resin in order to determine the amount of metal that was absorbed onto the column.

### **2.4 ICP-AES Analysis**

The eluate collected from the conclusion of each transition metal batch contact study was analyzed on a Thermo Scientific iCAP 7000 Series ICP-OES. The solutions were diluted with either 2% hydrochloric acid or 2% nitric acid, depending on the acid system, in 15 mL centrifuge tubes to achieve a maximum concentration of 1 ppm of the metal analyte.

## **3. Results and Discussion**

### **3.1 First Row Transition Metal Salt Solutions**

The amount of transition metal that was introduced into the system as a metal chloride/ nitrate salt was based upon the working capacity of Actinide Resin for other divalent (Ba(II):  $0.328\text{ mmol/g resin}$ ) and trivalent (Nd(III):  $0.315\text{ mmol/g resin}$ ) metal ions:

*Divalent metal ions M(II):*

$$0.0500 \text{ g resin} \frac{0.328 \text{ mmol Ba(II)}}{1 \text{ g resin}} \frac{1 \text{ mmol M(II)}}{1 \text{ mmol Ba(II)}} = 0.0164 \text{ mmol M(II)}$$

$$0.0164 \text{ mmol M(II)} / 0.0013 \text{ L acid} = 12.615 \text{ mM M(II)}$$

*Trivalent metal ions M(III):*

$$0.0500 \text{ g resin} \frac{0.315 \text{ mmol Nd(II)}}{1 \text{ g resin}} \frac{1 \text{ mmol M(II)}}{1 \text{ mmol Nd(II)}} = 0.01575 \text{ mmol M(III)}$$

$$0.01575 \text{ mmol M(III)} / 0.0013 \text{ L acid} = 12.115 \text{ mM M(III)}$$

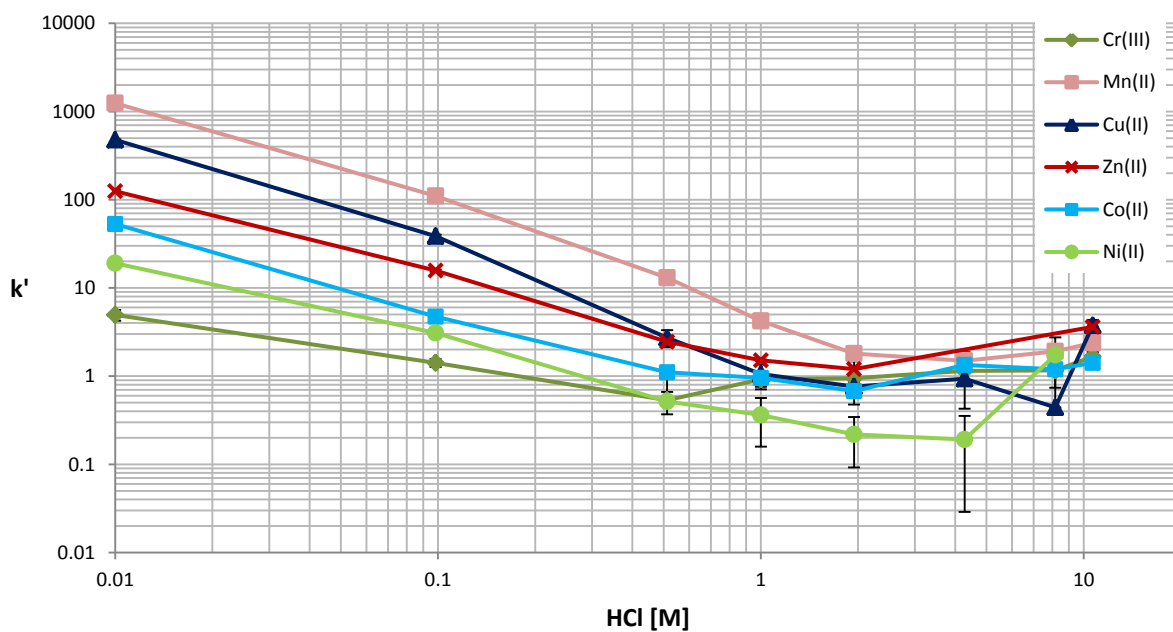
The maximum working capacity of Actinide Resin for divalent and trivalent metal ions was calculated to be 12.615 mM and 12.115 mM respectively. Therefore, a lower concentration of metal analyte (5 mM) was used within the batch contact studies in order to not overload the Actinide Resin.

### 3.2 Batch Experiment & ICP-AES Analysis

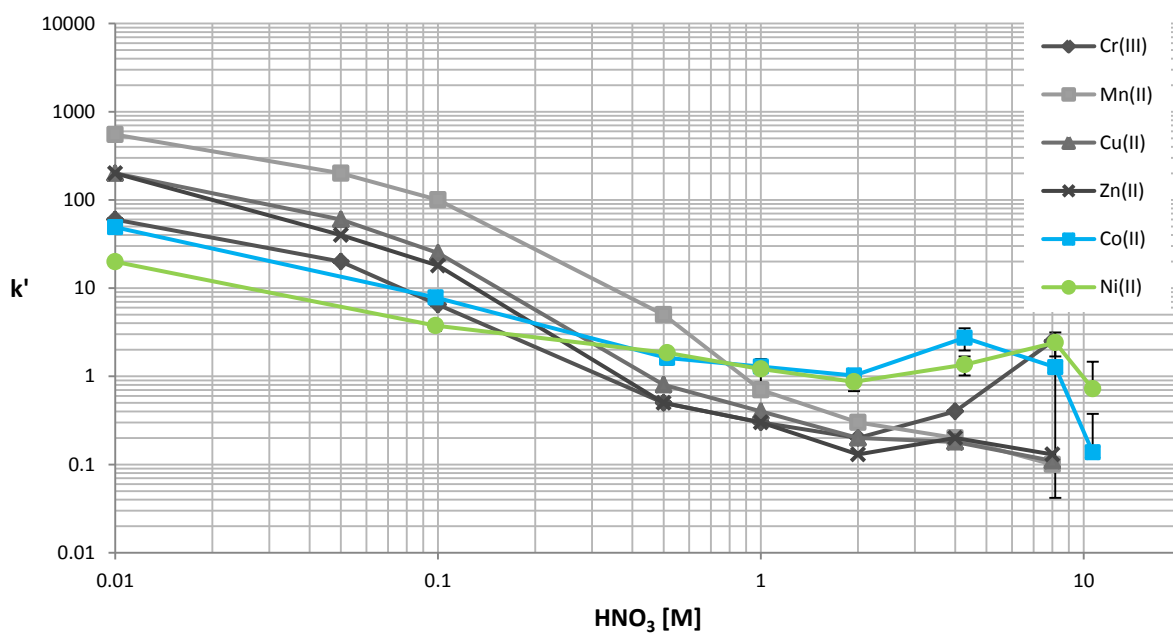
Batch contact studies were conducted in order to determine the retention capability of Actinide Resin for the first row transition metals. The retention factor,  $k'$ , values for the transition metals Cr(III), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) on Actinide Resin in varying concentrations of hydrochloric acid are depicted in Figure 5. The first row transition metals are more strongly retained below 0.1 M HCl, after which the retention diminishes with increasing acid concentration. Little selectivity is exhibited among the first row transition metals at varying concentrations of hydrochloric acid. The retention of divalent first row transition metals on Actinide Resin is stronger compared to trivalent metals; these results are unexpected for Actinide Resin which usually displays extremely high retention factors for metals that are trivalent.

The retention factor,  $k'$ , values for the transition metals Cr(III), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) on Actinide Resin in varying concentrations of nitric acid are depicted in Figure 6. Published research by McAlister et al. has already studied the absorption of Cr(III), Mn(II), Cu(II), and Zn(II) on Actinide Resin in varying concentrations of nitric acid (Figure 6: Gray Scale). The first row transition metals are more strongly retained below 0.1 M HNO<sub>3</sub>, after which the retention diminishes with increasing acid concentration. Similarly to the hydrochloric acid system, little selectivity was exhibited among the first row transition metals at varying concentrations of nitric acid.

The first row transition metals are more strongly retained in lower acid concentrations; therefore, large amounts of these metal ions within a sample could interfere with the uptake of actinide metal ions or could interfere with ICP-AES analysis.



**Figure 5:**  $k'$  values for first row transition metals in varying concentrations of HCl, 1 h equilibration time, 22 °C.



**Figure 6:** (Color)  $k'$  values for first row transition metals in varying concentrations of HNO<sub>3</sub>, 1 h equilibration time, 22 °C.

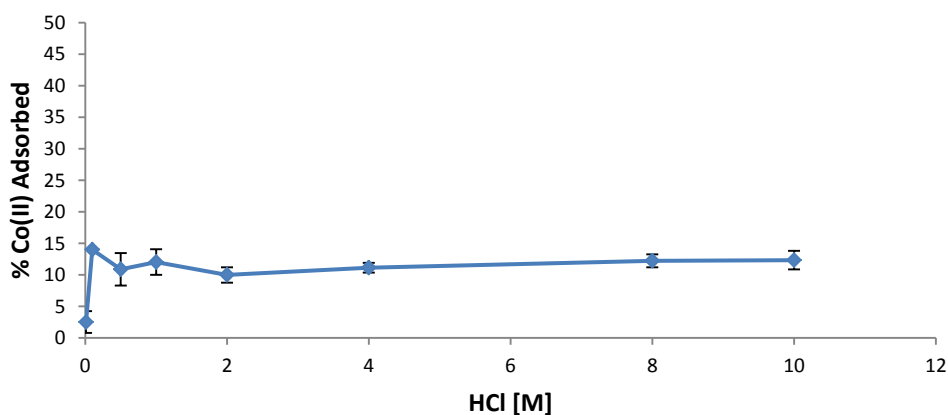
(Gray) Literature  $k'$  values for first row transition metals in varying concentrations of HNO<sub>3</sub>, 1 h equilibration time, 22 °C.<sup>2</sup>



Actinide Resin can have a specific affinity toward the mineral acid used. The amount of liquid that is being adsorbed onto the resin can affect the accuracy of the retention factor values. Therefore, volume correction factors for each mineral acid were determined for the Actinide Resin. The amount of solution that was taken up by the resin was determined by the weight of the eluate and the density of the solution. The volume correction factors for the resin reflected the change of volume induced by contact with the resin. Titrations of the acid samples were performed in order to determine the change in acid concentration after contact with the resin (Table 1). The change in acidity due to the Actinide Resin having an affinity for the acid was statistically significant for higher concentrations of the mineral acids (8-12 M), while the lower mineral acid concentrations did not statistically change.

Table 1: Mineral Acid Concentrations					
HCl [M]	HCl [M] After Resin Contact	Moles Adsorbed by Actinide Resin	HNO <sub>3</sub> [M]	HNO <sub>3</sub> [M] After Resin Contact	Moles Adsorbed by Actinide Resin
0.010 ± 0.000	0.013 ± 0.004	---	0.011 ± 0.001	0.020 ± 0.007	---
0.098 ± 0.003	0.09 ± 0.02	---	0.123 ± 0.003	0.115 ± 0.010	---
0.51 ± 0.06	0.4 ± 0.1	---	0.53 ± 0.01	0.61 ± 0.08	---
1.000 ± 0.000	1.1 ± 0.1	---	1.03 ± 0.03	1.1 ± 0.1	---
1.94 ± 0.10	1.96 ± 0.07	---	2.06 ± 0.10	2.1 ± 0.1	---
4.28 ± 0.07	4.3 ± 0.3	---	4.2 ± 0.2	4.0 ± 0.1	---
8.2 ± 0.3	7.57 ± 0.09	0.000773	8.3 ± 0.8	7.9 ± 0.2	0.000599
10.7 ± 0.3	9.41 ± 0.09	0.001635	12.7 ± 0.3	10.9 ± 0.1	0.002287

A resin blank batch contact study, in which the Bio-Spin Columns contained no Actinide Resin, was performed with Co(II) as the metal analyte in order to determine if the amount of metal that was adsorbed onto the column depended on the mineral acid concentration (Figure 7). The results indicated that the amount of Co(II) that was adsorbed onto the empty columns did not significantly change above 0.01 M HCl. However, the amount of Co(II) that was adsorbed onto the column was significant compared to other metal ions studied with an average of  $40 \pm 10$  ppm Co(II) being absorbed onto the column. The Empty Bio-Spin Chromatography Columns are polypropylene spin columns with polyethylene bed supports. Transition metal atoms are adsorbed more sensitively to polyethylene surfaces, in which the metal atoms appear with free electron pairs that binds the metals with co-ordination bonds<sup>6</sup>. Therefore, the amount of transition metal that adsorbed onto the column cannot be neglected when determining retention factor values of first row transition metals.



**Figure 7:** Co(II) adsorption on polyethylene Empty Bio-Spin Chromatography Columns in varying concentrations of HCl.

#### 4. Conclusions

Actinide Resin was further characterized for the first row transition metals that could be found within post-detonation debris or could interfere with ICP-AES analysis. Batch contact studies were conducted in order to determine the retention capability of Actinide Resin for unpublished first row transition metals. The first row transition metals are more strongly retained below 0.1 M HCl/ HNO<sub>3</sub>, after which the retention diminishes with increasing acid concentration. Also, little selectivity is exhibited among the first row transition metals at varying mineral acid concentrations.

#### 5. References

1. Horwitz, E.; Chiarizia, R.; Dietz, M.L. "DIPEX: A New Extraction Chromatographic Material for the Separation and Preconcentration of Actinides from Aqueous Solution", *Reactive & Functional Polymers*, **33** (1997), 25-36
2. McAlister, D. R.; Horwitz, E. P. "A method for the separation of beryllium from spectral interfering elements in inductively coupled plasma-atomic emission spectroscopic analysis" *Talanta*, **67** (2005), 873-879.
3. Braun, T.; Ghersini, G. *Extraction Chromatography*; Amsterdam: Elsevier Scientific Pub. Co, 1975.
4. *Extraction Chromatographic Resins*; Triskem International, Bruz, France.
5. Glasstone, S.; Dolan, P. J. *The Effects of Nuclear Weapons*, 3<sup>rd</sup> ed.; United States Department of Defense, 1977.
6. Lehto, J.; Hou, X. *Chemistry and Analysis of Radionuclides: Laboratory Techniques and Methodology*; John Wiley & Sons, 2011.